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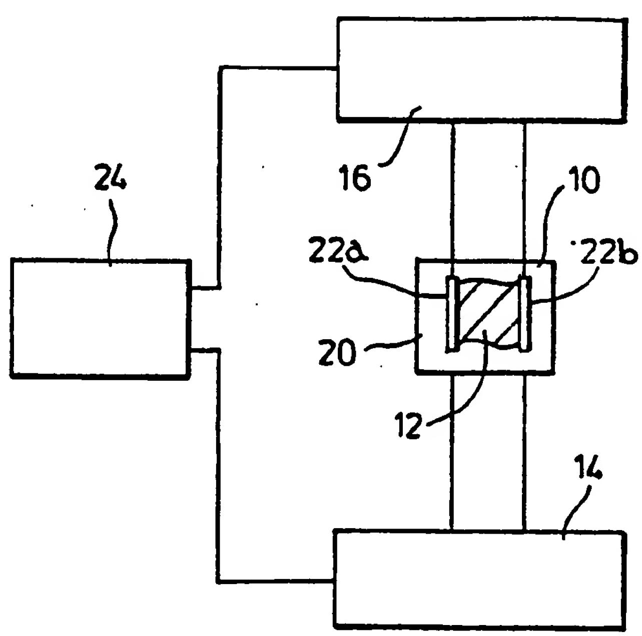
(57) Abstract

There is disclosed a gas sensing device comprising a mass measurement gas sensor coated with at least one layer of semiconducting organic polymer and having both mass measurement and conductimetric transduction means.

pizoelectric quartz crystal



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INTEGRATED SENSOR

This invention relates to gas sensors, in particular to gas sensors which combine mass measurement and conductimetric detection facilities, thereby permitting two transduction techniques to be applied to a single sensor.

The past decade has witnessed an upsurge of scientific and commercial interest in the development of sensors capable of detecting gases, vapours and odours. The result has been the emergence of a suite of detection techniques, possessing differing and often complementary characteristics.

Sensors based on quartz resonators and surface acoustic wave (SAW) devices may be referred to , broadly, as "mass measurement" techniques, since sensors of this kind are sensitive to, essentially, the mass of the gas adsorbed onto the active surface of the sensor. Quartz resonator sensors consist of a piezoelectric quartz crystal oscillator coated with a sensing membrane. In this instance, the increase in mass due to the adsorption of gaseous molecules onto the membrane results in a decrease in the resonant frequency : it is this frequency shift which is typically detected, although the response time constant may also be measured. SAW devices consist of a piezoelectric substrate (such as quartz) having interdigitated electrodes fabricated thereon, and a thin film coating of a sensitive material. A radio frequency voltage is applied across the electrodes which leads to the formation of a Rayleigh surface acoustic wave, the frequency of which is perturbed by the adsorption of gas due to the attendant increase in mass of the coating. SAW devices can be operated at higher frequencies than quartz resonator devices resulting in improvements in sensitivity.

In both instances the selectivity of the sensor is determined by the coating material, which is typically a polymer that shows absorptive characteristics that are useful for the range of molecules to be detected. Other materials have also been

employed as coatings for quartz resonators, such as celluloses, gas chromatographic stationary phase materials and both natural and synthetic lipids.

Another type of gas sensor, which is finding widespread application, involves the bridging of electrodes with semiconducting organic polymers (SOPs). The electrical properties of the polymer may be modified by the adsorption of gaseous species and therefore the presence of these species may be detected by monitoring the change in an electrical property accompanying the adsorption process. The electrical property may be the dc resistance of the polymer (see, for example, K.C. Persaud and P. Pelosi, Gas sensors: towards an artificial nose, in "Sensors and Sensory Systems for Advanced Robots", NATO ASI Series: Series F: Computer and Systems Science, ed. P. Dario, Springer-Verlag, Berlin, 1988, pp 361-382) or an ac impedance property such as conductance (see, for example, UK Patent GB 2203553, assigned to the present applicants). Sensors of this type offer a number of advantages including enhanced sensitivities compared to quartz resonator and SAW devices and rapid and reversible adsorption kinetics.

The "conductimetric" SOP based sensors and "mass measurement" sensors such as quartz resonators and SAWs may be regarded, to some extent, as complementary techniques. This is because the former, although possessing superior sensitivites, are only selective towards gases which adsorb onto the polymer **and** affect the electrical properties thereof. Such gases are generally polar molecules. The latter is selective toward all molecules which adsorb onto the active surface with an affinity which exceeds the inherent detection limit of the device.

The present invention provides an integrated sensor which combines both mass measurement and conductimetric transduction techniques in a single device. The most relevant prior art in this regard appears to be constituted by a series of papers by JM Slater et al (see, for example, J.M. Slater, E.J. Watt, N.J. Freeman, I.P. May and D.J.

Weir, Analyst, 117 (1992) 1265 and references therein) wherein a quartz resonator was coated with a SOP and mass measurements were made, augmented by conductimetric interrogation of a separate SOP sensor of the type described above.

It is understood that "gas sensing" includes the detection of volatile species.

According to the invention there is provided a gas sensing device comprising a mass measurement gas sensor coated with at least one layer of semiconducting organic polymer (SOP) and having both mass measurement and conductimetric transduction means.

The mass measurement gas sensor may be a quartz resonator device or a SAW device.

The conductimetric transduction means may comprise means for applying a dc electric signal across the layer or layers of SOP, and detection means for detecting changes in resistance.

Alternatively, the conductimetric transduction means may comprise means for applying an ac electric signal across the layer or layers of SOP, and detection means for detecting an impedance property.

The SOP may be deposited electrochemically, by oxidative chemical vapour deposition, or by spin or spray coating.

Contact electrodes may be bonded onto the SOP.

Embodiments of the invention will now be described with reference to the accompanying drawings, in which:-

Figure 1 is a schematic diagram of the apparatus together with a view from above the SAW device; and

Figure 2 is a view from below the SAW device.

Figures 1 and 2 depict a gas sensing device of the present invention comprising a mass measurement sensor 10 coated with a layer of SOP 12, and having both mass measurement transduction means 14 and conductimetric transduction means 16.

In one embodiment the mass measurement sensor 10 is a SAW device having interdigitated electrodes 18a, 18b fabricated onto a piezoelectric substrate 20 such as quartz. The mass measurement transduction means 14 includes rf voltage applying means for applying said voltage across the elecrodes 18a, 18b. The applied voltage produces a Rayleigh surface acoustic wave (i.e. a surface oscillation), the frequency of which is perturbed by changes in the mass of the sensor due to adsorption of gas onto the SOP coating. This frequency shift produces a voltage phase shift which may be detected by phase sensitive detection means. Said phase sensitive detection means may be part of the voltage applying means or a separate unit. In order to compensate for, eg, temperature and pressure variations the sensor 10 may be connected to a reference sensor and the frequency difference measured.

The layer of SOP 12 bridges two electrodes 22a, 22b, and the conductimetric transduction means 16 includes means for applying an electric signal across these electrodes. The electric signal may be a dc signal, in which instance the

transduction means 16 also includes resistance measuring means (such as described in, for example, BA Gregory; "An Introduction to Electrical Instrumentation and Measurement Systems", 1982, MacMillen). Alternatively, an ac electric signal may be applied, and an impedance property of the SOP layer 12, such as conductance, monitored. In this latter embodiment a rf impedance analyser could serve as the conductimetric transduction means 16. In either instance the presence of a gas is detected by detecting the variation in the electrical property monitored caused by adsorption of the gas onto the polymer.

Data from both transduction techniques may be transmitted, via a suitable interface , to a computer 24 for display and analysis purposes.

The advantage of the present invention is that the complementary properties of two gas sensing methods are combined <u>in one</u> device; in particular this feature permits the detection of both polar and non-polar molecules. The conductimetric method has relatively high sensitivity, but is only applicable to molecules which, in addition to being adsorbed onto the polymer, significantly affect the conductivity thereof. Generally speaking, such molecules are polar. The mass measurement method requires only that there is significant adsorption, since the measured properties depend upon the mass of the adsorbed material, and therefore non-polar molecules - which are readily absorbed onto the surface of the SOP - may be detectable. Thus it is contemplated that a single sensor may detect polar molecules at high sensitivities and, additionally, that hydrophobic interactions due to the adsorption of certain non-polar molecules will also be detectable by mass measurement techniques, even though the changes in SOP conductance associated therewith are of insufficient magnitude for detection by conventional SOP sensors. The precise identity of molecules detectable by either method depends upon the nature of the SOP used. It should be noted that the results of the two transduction techniques - whether or not there is a significant response- can be used in combination to provide extra information on the nature of the gas detected. It should also

be noted that whilst the foregoing discussion focusses upon the detection of a single gaseous species, the detection of mixtures of gases, vapours and odours, by a single sensor or by a plurality of sensors, is within the scope of the invention.

The SOP layer may be deposited by any of the numerous techniques described in the literature, such as electrochemical or oxidative chemical vapour deposition, or by spin or spray coating. Numerous SOPs have previously been employed for gas sensing purposes, polypyrrole being perhaps the most commonly encountered example, and the present invention is not limited in scope in this respect.

The contact electrodes 22a, 22b may be bonded to the piezoelectric substrate - such is necessary if an electrochemical deposition is contemplated - or may be bonded or attached to the SOP itself.

In a second embodiment of the invention a SOP coated quartz resonator device was produced by modification of a commercially available quartz resonator. The resonator is a quartz wafer having a layer of aluminium of approximate thickness 0.02 μm deposited on both sides thereof. Aluminium of one face of the resonator was selectively removed by a hand painted etch comprising nitric, acetic and phosphoric acids. Polypyrrole was then deposited by an oxidative chemical vapour method over a substantial portion of the etched resonator surface. The resulting quartz resonator 30, shown in Figure 3, this comprises a quartz wafer 32, an aluminium coating 34 and a polypyrrole coating 36. The polypyrrole coating 36 extends for approximately 6mm, virtually from one side of the resonator 30 to another, and exhibits a resistance of ca. 10KΩ.

Electrical connections are made using commercially supplied spring contact electrodes (not shown). With such electrodes, the quartz wafer 32 is pressed between the windings of the spring contact. The contacts originally supplied with the

resonator were positioned in contact with the aluminium coating 34 towards the corners of the upper wafer edge ("upper" being defined with respect to Figure 3). Identical contacts, cannibalised from another commercial quartz resonator device, were similarly placed on the lower wafer edge, in contact with the polypyrrole coating 36.

The resonator was then housed within a PTFE block and connected to a vapour rig of straightforward design. The spring contact electrodes in contact with the aluminium coating 34 were connected to an impedance analyser and the reactance was measured around the resonant frequency (<u>ca.</u> 1845 KHz). Figure 4 shows the effect of exposing the resonator to dry air 1, ethanol vapour 2 and toulene vapour 3 at a flow rate of 200 ml min^{-1}. Frequency shifts (with respect to the dry air valve) of -33.5 Hz ethanol and -18.5 Hz for toulene are observed. Figure 5 shows the kinetic response of the resonator to a pulse of toulene vapour. A change of 1200% in the reactance (measured around 1844.91 KHz) is observed.

The frequency shift measurements are "mass measurements", because the observed perturbation of the resonant frequency is induced by the mass change due to adsorption of molecules with high affinity onto the polymer (although non-specific adsorption onto other regions of the resonator will likely play an as yet unquantified role). Conductimetric measurements were also made by connecting the spring contact electrodes in contact with the polpyrrole coating 36 to a dc resistance measuring meter of conventional type. The dc resistance of the resonator in a dry air atmosphere was 11.8Ω, which rose to 13.1Ω and 12.5Ω on exposure to ethanol and toluene vapour respectively. Thus it is possible to extract responses from two complementary transduction techniques using a single quartz resonator.

An improvement on the present arrangement would involve removal of part of the aluminium coating on one face of the resonator followed by patterning with a suitable gold electrode structure. A polymer, or, if desired, an array of polymers could

be deposited on and between the electrode structure. Conventional wire bonding techniques could be used to connect to the electrode structure, whilst the spring loaded connection method would be retained for connection to the aluminium coatings.

Similarly, arrays of quartz resonators or SAW devices, or combinations thereof, with different SOPs can be constructed. Patterns of responses from such arrays can be used to identify individual or complex mixtures of chemical species.

CLAIMS

1. A gas sensing device comprising a mass measurement gas sensor coated with at least one layer of semiconducting organic polymer and having both mass measurement and conductimetric transduction means.

2. A gas sensing device according to claim 1 in which the mass measurement gas sensor is a quartz resonator device.

3. A gas sensing device according to claim 1 in which the mass measurement gas sensor is a SAW device.

4. A gas sensing device according to any one of claims 1 to 3 in which the conductimetric transduction means comprise means for applying a dc electric signal across the layer or layers of semiconducting organic polymer, and detection means for detecting changes in resistance.

5. A gas sensing device according to any one of claims 1 to 3 in which the conductimetric transduction means comprise means for applying an ac electric signal across the layer or layers of semiconducting organic polymer, and detection means for detecting an impedance property.

6. A gas sensing device according to any of the previous claims in which the semiconducting organic polymer is deposited electrochemically, by oxidative chemical vapour deposition, by spin coating or by spray coating.

7. A gas sensing device according to any of the previous claims in which contact electrodes are bonded onto the semiconducting organic polymer.

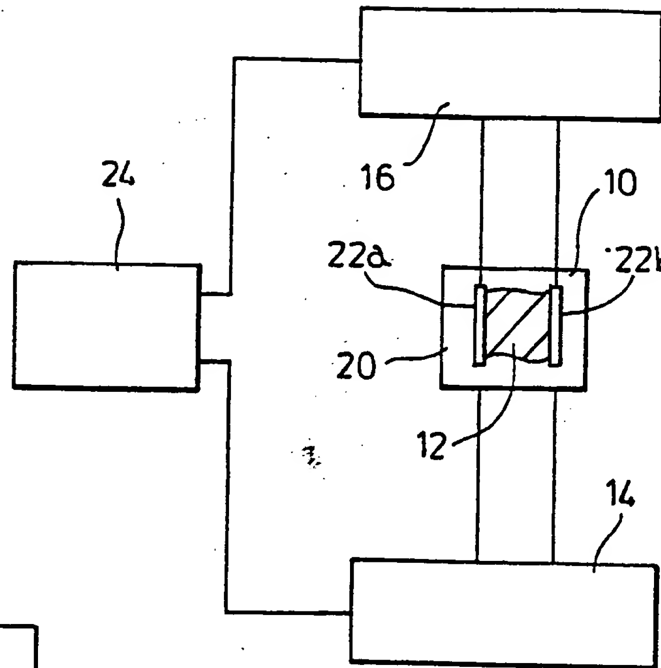

FIG.1

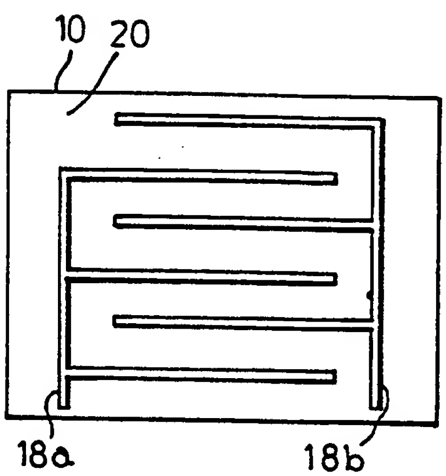

FIG.2

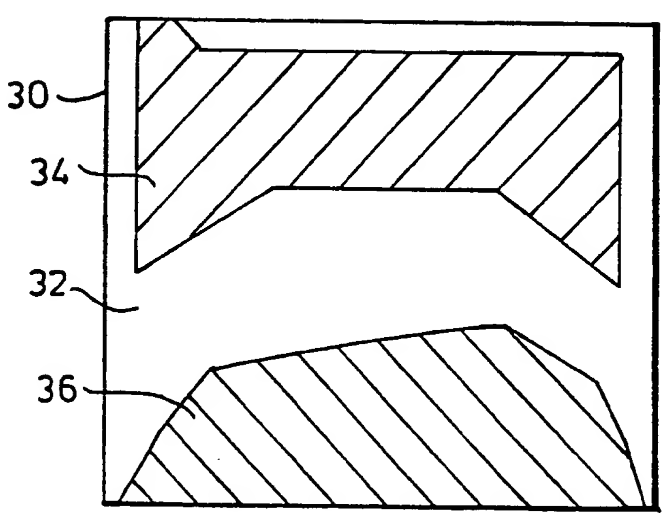

FIG.3

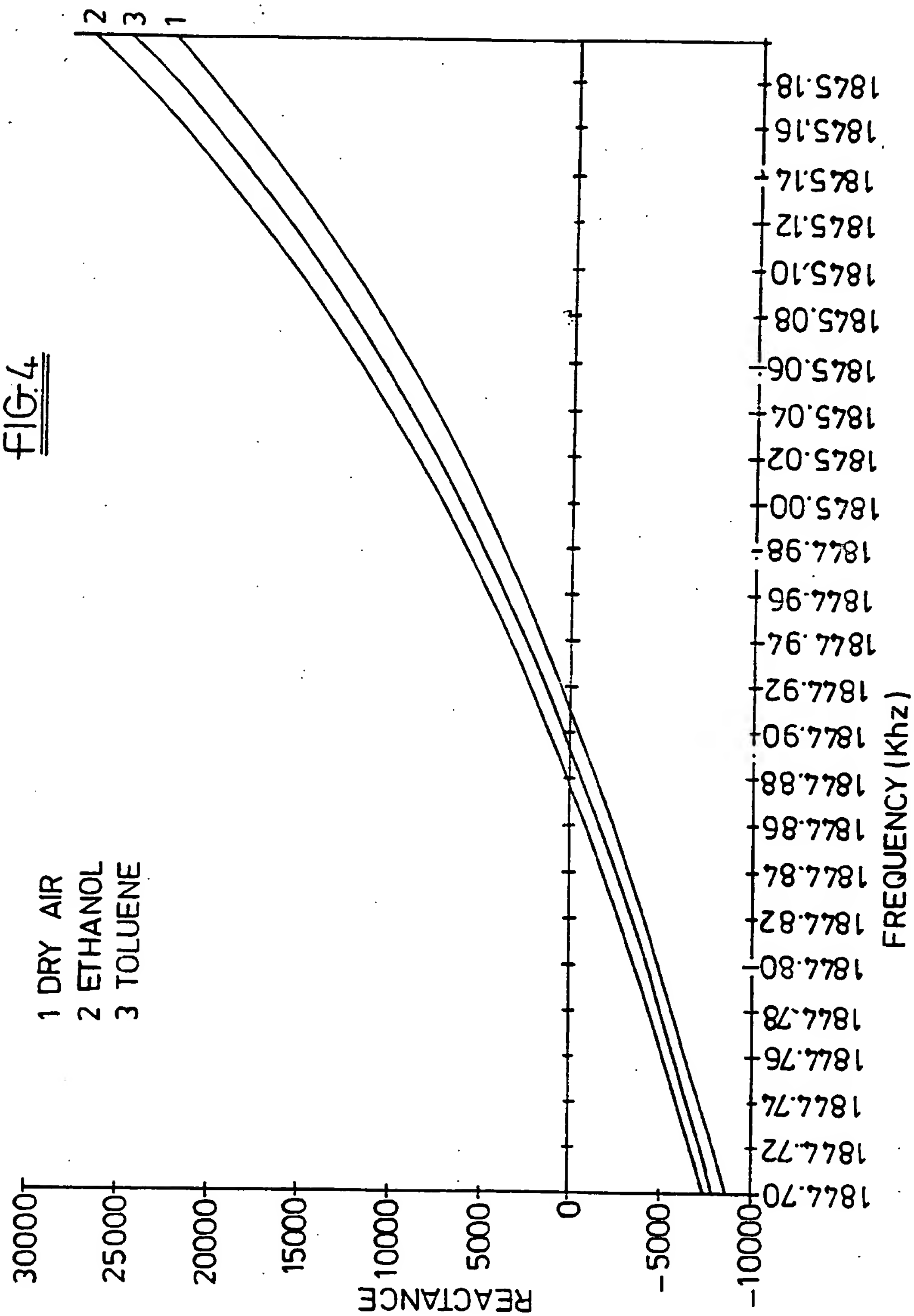
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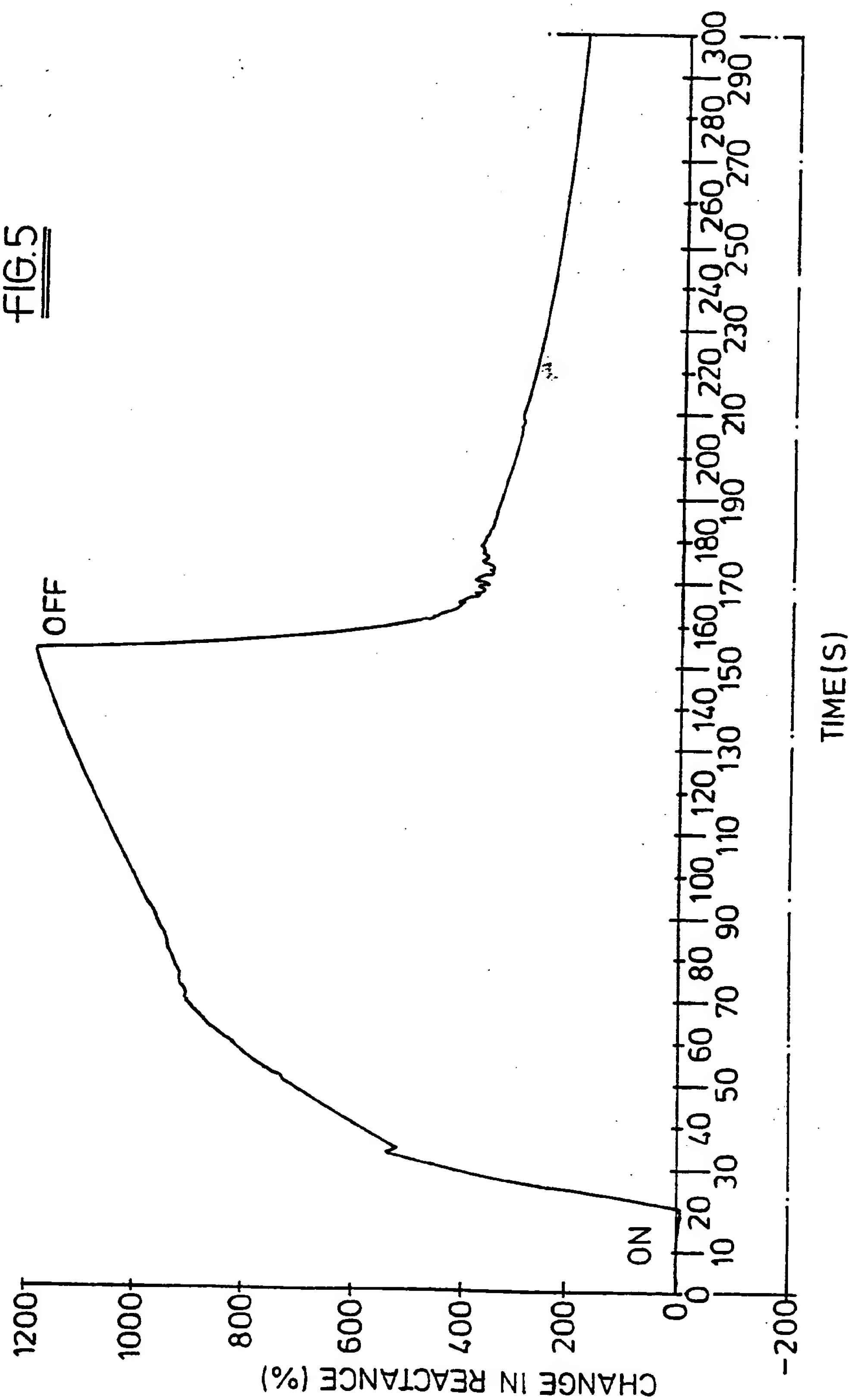
FIG. 4

FIG.5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INTERNATIONAL SEARCH REPORT

Int... onal Application No
PCT/GB 96/01339

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G01N27/12 G01N29/02 G01N27/00 G01N33/00

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G01N

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,4 681 855 (HUANG) 21 July 1987 see the whole document ---	1-7
Y	JAPANESE JOURNAL OF APPLIED PHYSICS, vol. 31, September 1992, TOKYO JP, pages 3070-3072, XP000355711 T. NOMURA ET AL.: "MEASUREMENT OF HUMIDITY USING SURFACE ACOUSTIC WAVE DEVICE" see the whole document ---	1-7
Y	ANALYST, vol. 117, August 1992, LONDON, GB, pages 1265-1270, XP000604336 J.M. SLATER, ET AL.: "GAS AND VAPOUR DETECTION WITH POLY(PYRROLE) GAS SENSORS" cited in the application see the whole document ---	1-7

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[X] Further documents are listed in the continuation of box C.

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A	PATENT ABSTRACTS OF JAPAN vol. 17, no. 666 (P-1656), 8 December 1993 & JP,A,05 223720 (NIPPON TELEGR & TELEPH CORP <NTT>), 31 August 1993, see abstract	1-7
A	WO,A,93 03355 (NEOTRONICS LIMITED) 18 February 1993 see page 2, line 24 - page 5, line 6	1,4-7
A	US,A,4 674 320 (HIRSCHFELD) 23 June 1987 see column 1, line 11 - column 2, line 4	1-7

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 96/01339

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		CA-A-	2113544	18-02-93
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		EP-A-	0596973	18-05-94
		JP-T-	6509869	02-11-94
US-A-4674320	23-06-87	NONE		